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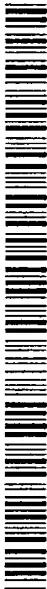


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(54) Title: POLYMERIZATION OF A REACTIVE DILUENT IN THE PRESENCE OF AN EPOXY-AMINE MATERIAL, AND COATING COMPOSITIONS PREPARED THEREBY

(57) Abstract: A process including the polymerization of a reactive diluent, which is present in an aqueous dispersion that further includes an epoxy-amine material, is disclosed. The resulting composition is useful as a coating composition.

5 POLYMERIZATION OF A REACTIVE DILUENT IN THE
PRESENCE OF AN EPOXY-AMINE MATERIAL, AND
COATING COMPOSITIONS PREPARED THEREBY

This application claims the benefit of U.S. Provisional Application No. 60/362,608, filed March 8, 2002, which is incorporated herein by reference in its 10 entirety.

BACKGROUND

Various coating compositions, methods for coating substrates with such compositions, and methods of curing the coated substrates are well known in the art. A coating composition is sometimes applied as a film, which may include a carrier (e.g., water and/or organic solvent). The coating may be applied on a substrate by a process such as lamination, solution or dispersion coating, powder coating, electrocoating, spray coating, roll coating, or reverse roll coating. Coating compositions can also be applied as a film by extrusion in melt form through an extrusion coating die onto a substrate. Once coated on the substrate, the composition is preferably cured (and dried if the composition includes a carrier) without defects within a few seconds, as modern high speed coating lines heat the coated substrates rapidly to temperatures of up to 490°F (254°C). Using such techniques, many different types of substrates have been coated including, for example, wood, plastics, and metal in the form of sheets, strips, or coils. Metal-coated substrates are especially useful in the packaging, processing, and holding of foods and beverages.

It is desirable to avoid the use of excess organic solvent in a coating method so that the environmental hazards of allowing organic solvent to 30 evaporate into the atmosphere are minimized. However, a relatively large quantity of organic solvent is typically required in order to process the coating composition and provide a coalesced film after drying.

Epoxy resins are particularly desirable for use in protective surface coating compositions, e.g., as a vehicle or polymeric binder for optional pigments, fillers, and other additives. The epoxy resins advantageously provide properties such as toughness, flexibility, adhesion, and chemical resistance.

5 A number of attempts have been made in the prior art to prepare aqueous, solvent based, or solvent free coating compositions suitable for use in a process for forming cured coated substrates. For example, container coating technology has utilized an epoxy resin that has been grafted with acrylic monomers, styrene, and methacrylic acid. This grafted epoxy resin is prepared in solvent, usually
10 butyl cellosolve and/or n-butanol, to maintain low processing viscosities, and then reduced with water by a direct or inverse let down procedure. Although the cured film properties are highly desirable, such coatings suffer from the fact that sizeable amounts of solvents are required to obtain good performance. High molecular weight epoxy resins typically require 25% to 50% solvent (based on
15 total solids plus organic solvent) before the composition is reduced with amine and water.

Another problem that commonly arises during attempted preparation of a water based coating composition is the formation of an extremely high molecular weight product that cannot be dissolved or dispersed in water. There is a
20 continuing need for aqueous coating compositions that can be applied to a substrate to provide excellent coating characteristics.

SUMMARY

In one aspect, the present invention provides a method of preparing a
25 coating composition, and coating compositions prepared thereby. The method includes the steps of making an aqueous dispersion of a composition including an advanced molecular weight epoxy-amine material and a reactive diluent, and polymerizing the reactive diluent to provide the coating composition. Preferably, the method further includes the step of combining an amine and an
30 epoxy material in the presence of a reactive diluent to provide the composition including an advanced molecular weight epoxy-amine material and a reactive diluent. Preferably, the step of making the aqueous dispersion includes

combining the composition with an acid. Preferably, the coating composition has a volatile organic compound content of at most 0.2 kilograms per liter of solids.

In another aspect, the present invention provides a method of coating an article. The method includes the steps of applying the above-described coating composition to an article and hardening the coating composition to provide a coated article. Preferably, the method includes the step of heating the coated article to provide a crosslinked coating.

Definitions

- 10 The terms related to coating compositions and methods for coating substrates are used in accordance with the understanding of one skilled in the art, unless otherwise noted. For example, the terms "coating solids" and "coating solids component" refer to the sum of the mass of components used in the composition (e.g., epoxy-amine material, reactive diluent, epoxy material, and 15 any other reactive curing agents, reactive diluent components, or initiators that are employed), exclusive of water or organic solvent. As used herein, "solvent" refers to a volatile liquid component of the composition that does not react during the curing or baking steps. Most of the solvent is generally volatilized during a baking step and does not become incorporated into the cured coating.
- 20 The organic solvent is typically made up of saturated organic compound(s) having a molecular weight of less than 300 Daltons.

As used herein, "advanced molecular weight epoxy-amine material" refers to the reaction product of an epoxy material (e.g., an epoxy resin) with an amine to provide an epoxy-amine material having increased (i.e., advanced) ← .25 molecular weight compared to the starting epoxy material. Preferably the epoxy-amine material has residual epoxy functionality.

- 30 "Polymerization" or "polymerizable" denotes the curing or cross-linking of the coating composition after a coated substrate is exposed to radiation (e.g., ultra-violet or electron beam), heat, or other means of initiating polymerization. "Thermosettable" or "thermoset" refers to a composition that is transformed into a gel structure by application of radiation and/or heat. A gel structure is one that is largely insoluble in any solvent.

As used herein, "volatile organic compound" ("VOC") refers to any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions. Typically, volatile organic compounds have a vapor pressure equal to or greater than 0.1 mm Hg. As used herein, "volatile organic compound content" ("VOC content") means the weight of VOC per volume of the coating solids, and is reported, for example, as kilograms (kg) of VOC per liter.

10 DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention provides a method of preparing an advanced molecular weight epoxy-amine material in the presence of a reactive diluent. The advanced molecular weight epoxy-amine material is preferably prepared by combining an amine with an epoxy material in the presence of a reactive diluent. The composition, which includes the advanced molecular weight epoxy-amine material and the reactive diluent, is useful for making a coating composition by making an aqueous dispersion of the composition, followed by polymerizing the reactive diluent.

EPOXY MATERIALS

20 Epoxy materials including, for example, epoxy resins or compounds, are materials containing epoxy groups. Epoxy materials used in the present invention may be prepared by a variety of processes including, for example, the condensation of a dihydroxy compound with epichlorohydrin. Dihydroxy compounds useful for preparing the epoxy materials include, for example, diphenols and dihydric alcohols. Preferred epoxy materials include, for example, materials derived from the condensation of Bisphenol A and/or Bisphenol F with epichlorohydrin.

25 Epoxy materials suitable for use in the present invention may be prepared according to known methods including those described in U.S. Pat. Nos. 4,446,258 (Chu et al.) and 4,476,262 (Chu et al.). Typically, epoxy materials are prepared by reacting one equivalent of Bisphenol A or Bisphenol F with the desired number of equivalents of epichlorohydrin to produce a material with

residual epoxy functionality (e.g., an epoxy resin). Suitable epoxy materials include, for example, those available under the trade designations EPON 828, EPON 1001, EPON 1004F, EPON 1007, EPON 1009 from Resolution Performance Products (Houston, TX). Commercially available epoxy materials 5 may contain a mixture including, for example, diepoxides, monoepoxides, and aromatic polyethers that are free of epoxy groups. Preferred epoxy materials have an epoxy equivalent weight (EEW) of at most 2000. Preferably, the epoxy material is capable of being dissolved in a reactive diluent.

Preferred epoxy materials include glycidyl end-capped poly(Bisphenol 10 A-*co*-epichlorohydrin), glycidyl end-capped poly(Bisphenol F-*co*-epichlorohydrin), glycidyl end-capped poly(Bisphenol F-*co*-epichlorohydrin)-*co*- (Bisphenol A-*co*-epichlorohydrin), poly(alkylene glycol) diglycidyl ether, poly(tetrahydrofuran) diglycidyl ether, and combinations thereof. Preferably, the poly(alkylene glycol) diglycidyl ether is poly(ethylene glycol) diglycidyl ether or 15 poly(propylene glycol) diglycidyl ether. Particularly preferred epoxy materials include, for example, those available under the trade designation EPON 1004F from Resolution Performance Products (Houston, TX)

AMINES

Amines useful for reacting with epoxy materials to form advanced 20 molecular weight epoxy-amine materials include materials having primary, secondary, and/or tertiary amine-functionality. Useful amines include monoamines, diamines, and polyamines. Examples of useful amines include those listed in U.S. Pat. No. 4,468,307 (Wismer et al.) Preferably, the amine has an amine equivalent weight of 22 to 300.

← 25 Preferred amines include monoamines (e.g., hydroxy-functional amines). Polyamines including, for example, ethylene diamine, diethylene triamine, triethylene tetraamine, N-(2-aminoethyl)ethanolamine, piperazine, and combinations thereof, may also be useful. However, when polyamines are used, preferably they are not used in large amounts because of their tendency to cause 30 gelation of reaction mixtures.

Preferred amines include secondary and tertiary amines. Primary amines may also be useful, however they may have a tendency to cause gelation of

reaction mixtures, since one equivalent of primary amine is capable of reacting with more than one equivalent of epoxy-functionality. When using polyamines and/or primary amines, special precautions may be taken to avoid gelation. For example, excess amine can be used and the excess can be vacuum stripped at the 5 completion of the reaction. Also, the epoxy material may be added to the amine to ensure that excess amine is present.

Useful hydroxy-functional amines include, for example, alkanolamines, dialkanolamines, trialkanolamines, alkylalkanolamines, arylalkanolamines, arylalkylalkanolamines, and combinations thereof, in which the alkanol, alkyl, 10 and/or aryl chains preferably contain 2 to 18 carbon atoms. Preferred hydroxy-functional amines include, for example, ethanolamine, N-methylethanolamine, diethanolamine, N-phenylethanolamine, N,N-dimethylethanolamine, N-methyldiethanolamine, triethanolamine, and combinations thereof.

Non hydroxy-functional amines (e.g., monoalkyl amines, dialkyl amines, 15 trialkyl amines, mixed alkyl-aryl amines, and substituted amines in which the substituents are other than hydroxy) may also be useful. If substituted amines are used, preferably the substituents do not detrimentally affect the reaction of the amine with the epoxy material. Preferred non hydroxy-functional amines include, for example, ethylamine, propylamine, methylethylamine, diethylamine, 20 N,N-dimethylcyclohexylamine, triethylamine, N-benzyldimethylamine, dimethylcocoamine, dimethyltallowamine, and combinations therof.

Other amines including, for example, hydrazine and propylene imine, may also be useful. Ammonia may also be useful, and for the purposes of this application is considered to be an amine. Combinations of the various amines ← .25 described above can also be used.

REACTIVE DILUENTS

Reactive diluents are used in conjunction with the epoxy materials to prepare the advanced molecular weight epoxy-amine materials and, ultimately, the coating compositions. As used herein, "reactive diluent" refers to monomers 30 and/or oligomers that are substantially non-reactive with the epoxy material and/or amine under the conditions used to prepare the epoxy-amine material. Reactive diluents useful in the present invention are preferably capable of

undergoing a reaction to form a polymer and/or an interpenetrating network. Reactive diluents useful in the present invention include, for example, monomers and/or oligomers that are capable of undergoing free radical reactions.

Preferably, the reactive diluent has a molecular weight of 100 Daltons to 350

5 Daltons.

Useful reactive diluents include monofunctional and multifunctional reactive diluents. Preferred reactive diluents include vinyl compounds, methacrylate compounds, and combinations thereof.

When the reactive diluent is a vinyl compound, the vinyl compound is
10 preferably a vinyl aromatic compound. Useful vinyl aromatic compounds include, for example, styrene, substituted styrenes, and combinations thereof.

The reactive diluent may also be a methacrylate compound. Preferred methacrylate compounds include, for example, butylmethacrylate, methyl methacrylate, ethyl methacrylate, isobutyl methacrylate, 2-hydroxyethyl
15 methacrylate, isobornyl methacrylate, poly(ethylene glycol) methacrylate, poly(propylene glycol) methacrylate, and combinations thereof.

Preferably, the reactive diluent functions as a solvent to dissolve, disperse, or otherwise lower the viscosity of the materials used in the preparation of the epoxy-amine material. Although the use of a reactive diluent preferably
20 reduces or eliminates the need to use substantial amounts of a solvent, solvents may nonetheless be added as desired.

Additional reactive diluents may also be used in combination with the reactive diluents described above. The additional reactive diluents may be introduced anytime before polymerizing the reactive diluents. Preferably, they
25 are introduced after making the aqueous dispersion.

Additional reactive diluents may be monofunctional or multifunctional reactive diluents. Useful additional reactive diluents, in addition to the reactive diluents described above, include, for example, acrylate compounds. Useful acrylate compounds include, for example, butyl acrylate, ethyl acrylate, 2-
30 ethylhexyl acrylate, isobutyl acrylate, *tert*-butyl acrylate, 2-hydroxyethyl acrylate, poly(ethylene glycol) acrylate, isobornyl acrylate, glycidyl acrylate, glycidyl methacrylate, acrylic acid, and combinations thereof.

ADVANCED MOLECULAR WEIGHT EPOXY-AMINE MATERIAL

- Advanced molecular weight epoxy-amine materials may be prepared by combining an amine with an epoxy material in the presence of a reactive diluent. Preferably, at least 0.1 equivalent of amine, more preferably at least 0.2 5 equivalent of amine, and most preferably at least 0.3 equivalent of amine is combined with each equivalent of epoxy material. Preferably, at most 1.05 equivalents of amine, more preferably at most 1 equivalent of amine, and most preferably at most 0.95 equivalent of amine is combined with each equivalent of epoxy material.
- 10 Preferably, at least 7.5% by weight, more preferably at least 15% by weight, and most preferably at least 20% by weight reactive diluent is used based on the total combined weight of epoxy material, amine, and reactive diluent. Preferably, at most 80% by weight, more preferably at most 50% by weight, and most preferably at most 30% by weight reactive diluent is used 15 based on the total combined weight of epoxy material, amine, and reactive diluent.

An example of a convenient procedure for preparing advanced molecular weight epoxy-amine material is to first dissolve the epoxy material in the reactive diluents. Preferably, the epoxy material dissolves at a temperature of at 20 most 130°C, more preferably at most 120°C, and most preferably at most 110°C. The materials may be agitated as desired to assist in the dissolution.

When using some reactive diluents, it may be desirable to prevent the reactive diluent from polymerizing at the dissolution temperatures. Convenient methods of preventing the polymerization include, for example, maintaining an oxygenated condition and/or adding antioxidants and/or inhibitors. Preferred 25 inhibitors include, for example, 2,6-di-*tert*-butyl-4-methylphenol. When antioxidants and/or inhibitors are used, they are preferably used in at least 0.01% by weight based on the total combined weight of epoxy material, amine, and reactive diluent. When antioxidants and/or inhibitors are used, they 30 are preferably used in at most 0.5% by weight based on the total combined weight of epoxy material, amine, and reactive diluent.

After the epoxy material has been dissolved in the reactive diluent, the temperature of the mixture may be adjusted (e.g., cooled) to the desired temperature for addition of the amine. After the addition of the amine, the temperature of the mixture may be adjusted as desired to allow the reaction to take place. Preferably, the reaction temperature is at most 130°C, more preferably at most 120°C, and most preferably at most 110°C.

When the amount of amine used is low (e.g., the ratio of equivalents of amine to equivalents of epoxy material is less than 1), advanced molecular weight epoxy-amine material having residual epoxy functionality may be prepared. The residual epoxy functionality may hydrolyze during the preparation of the aqueous dispersion to provide hydroxy functionality, which can be used, for example, to react with suitable crosslinkers.

Alternatively, advanced molecular weight epoxy-amine materials having residual epoxy functionality may be reacted with active hydrogen compounds (e.g., as described below) to further advance the molecular weight of the epoxy-amine material. The reaction of an active hydrogen compound with an advanced molecular weight epoxy-amine materials having residual epoxy functionality may be carried out before making the aqueous dispersion, after making the aqueous dispersion, or after polymerizing the reactive diluent as desired.

Preferably, at most 1.05 equivalents of active hydrogen compound, more preferably at most 1 equivalent of active hydrogen compound, and most preferably at most 0.95 equivalent of active hydrogen compound are used per equivalent of residual epoxy functionality.

ACTIVE HYDROGEN COMPOUNDS

As used herein, active hydrogen compounds and/or precursors (i.e., compounds that may form active hydrogen compounds) are compounds that include at least one hydrogen atom that may be readily dissociated in an aqueous environment. Preferably, the hydrogen atom is attached to a nitrogen atom, an oxygen atom, a phosphorous atom, or a sulfur atom.

Useful active hydrogen compounds and/or precursors in which the active hydrogen is attached to nitrogen include, for example, amines, diamines,

polyamines, hydrazides, dihydrazides, polyhydrazides, ketimines, diketimines, polyketimines, and combinations thereof.

Useful active hydrogen compounds in which the active hydrogen is attached to oxygen include, for example, dicarboxylic acids, polycarboxylic acids, bisphenols, polyphenols, and combinations thereof.

Useful active hydrogen compounds in which the active hydrogen is attached to sulfur include, for example, mercaptans, dimercaptans, polymercaptans, and combinations thereof.

Preferred active hydrogen compounds include, for example, 3-mercaptopropionic acid, 2-mercptoethanol, adipic dihydrazide, hydrazine, ammonia, ethylenediamine, N-(2-aminoethyl)ethanolamine, diethylenetriamine, triethylenetetramine, diethanolamine, bisphenol A, bisphenol F, N-ethylethylenediamine, 1,4-butanedithiol, propyleneimine, N,N'-dimethyl-1,6-hexanediamine, 1,6-hexanediamine, and combinations thereof.

15 CROSSLINKERS

Crosslinkers may be incorporated into the coating composition to enhance the crosslinking that occurs during the cure of coating composition after being coated on a substrate and dried. Crosslinkers include materials that are capable of reacting with other functionalities present in the coating composition at the curing temperature.

Examples of suitable crosslinkers include amines, melamines, blocked isocyanates, glyco-uryls, ketimines, epoxies, and combinations thereof.

Preferred crosslinkers include, for example, blocked isocyanates available under the trade designation VESTANAT 31358/100 from DeGussa Corp. (Parsippany, NJ).

SURFACTANTS

Surfactants may optionally be used to aid in the preparation of the dispersion. Useful surfactants include, for example, cationic surfactants, nonionic surfactants, and combinations thereof, as described, for example, in 30 *McCutcheon's, Volume 1: Emulsifiers & Detergents, North American Edition (2001)*. Useful cationic surfactants include, for example, ethoxylated amines, ethoxylated fatty amines, quaternary ammonium compounds, and combinations

thereof. A preferred cationic surfactant is described in U.S. Pat. No. 4,468,307 (e.g., column 9, lines 60-65). Useful nonionic surfactants include, for example, ethoxylated alkylphenols, ethoxylated fatty alcohols, ethoxylated alcohols, and combinations thereof. The surfactant may optionally include a polymerizable 5 ethylenically unsaturated functionality.

When a surfactant is used, preferably at least 0.1% by weight, more preferably at least 0.2% by weight, and most preferably at least 0.5% by weight surfactant is used, based on the total weight of the coating solids. When a 10 surfactant is used, preferably at most 5% by weight, more preferably at most 3% by weight, and most preferably at most 2% by weight surfactant is used, based on the total weight of the coating solids.

OTHER COATING ADDITIVES

Solvents may optionally be added to the coating compositions provided by the present invention as desired. A wide variety of solvents are suitable for 15 use in the present invention. However, as previously mentioned, the use of substantial amounts of solvents may contribute to an undesirably high level of volatile organic compounds that might have to be removed or recovered.

Useful solvents include, for example, aromatic solvents (e.g., xylene, toluene), alcohols (e.g., butanol and amyl alcohol), ethyleneglycol ethers (e.g., 2- 20 butoxyethanol and 2-hexyloxyethanol), propyleneglycol ethers, ketones (e.g., acetone and methyl isobutyl ketone), amides (e.g., 1-methyl-2-pyrrolidinone and N,N-dimethylformamide), and combinations thereof. Preferred solvents include, for example, 1-methyl-2-pyrrolidinone and N,N-dimethylformamide. When a solvent is used, preferably at most 20% by weight, more preferably at most 10% 25 by weight, and most preferably at most 5% by weight solvent is used, based on the total weight of the coating solids.

Other additives may be added to coating compositions provided by the present invention as desired. Examples of such additives include, for example, dyes and pigments, viscosity modifiers, defoamers, ultraviolet light (UV) 30 absorbers, wetting agents, fillers, dispersants, and combinations therof.

AQUEOUS DISPERSIONS

Aqueous dispersions of the advanced molecular weight epoxy-amine material may be prepared by acidifying a composition including the advanced molecular weight epoxy-amine material. Acids useful for acidifying the 5 composition are described herein below.

In one embodiment, the advanced molecular weight epoxy-amine material may be combined with an aqueous acid to provide an aqueous dispersion of the advanced molecular weight epoxy-amine material. Optionally, a surfactant may be used to aid in the formation of the aqueous dispersion. The 10 surfactant may be added to the advanced molecular weight epoxy-amine material either before or after the material is combined with the aqueous acid.

Alternatively, the aqueous acid may include a surfactant.

In another embodiment, the advanced molecular weight epoxy-amine material may be acidified with an acid, and the resulting acidified composition 15 may be combined with an aqueous liquid to provide an aqueous dispersion of the advanced molecular weight epoxy-amine material. Optionally, a surfactant may be used to aid in the formation of the aqueous dispersion. The surfactant may be added to the advanced molecular weight epoxy-amine material either before or after acidification with the acid. Alternatively, the aqueous liquid may include a 20 surfactant.

Preferably, sufficient acid is used to provide the desired degree of neutralization of the amine. Preferably, sufficient acid is used to provide at least 0.3 equivalent of acid per equivalent of amine, more preferably at least 0.5 equivalent of acid per equivalent of amine, and most preferably at least 0.6 ← . 25 equivalent of acid per equivalent of amine. Preferably, sufficient acid is used to provide at most 1.5 equivalents of acid per equivalent of amine, more preferably at most 1.2 equivalents of acid per equivalent of amine, and most preferably at most 1 equivalent of acid per equivalent of amine.

ACIDS

30 The acid used to make the aqueous dispersion is preferably an aqueous acid. The acid may be an organic acid or an inorganic acid. Examples of useful acids include, for example, carboxy-containing acids, phosphorous-containing

acids, sulfur-containing acids, hydrochloric acid, and combinations thereof. Preferably, the acid is soluble in water. Preferably, the acid is a non-volatile material.

Exemplary carboxy-containing acids include, for example, lactic acid, 5 formic acid, acetic acid, dimethylolpropionic acid, erythorbic acid, ascorbic acid, isophthalic acid, phthalic acid, terephthalic acid, maleic acid, succinic acid, propionic acid, acrylic acid, methacrylic acid, carbonic acid, oxalic acid, adipic acid, and combinations thereof.

Exemplary phosphorous-containing acids include, for example, 10 phosphoric acid, phosphoric acid derivatives, and combinations thereof.

Exemplary sulfur-containing acids include, for example, sulfuric acid, sulphonic acid, sulfamic acid, sulfamic acid derivatives, and combinations thereof

POLYMERIZATION OF REACTIVE DILUENTS

15 Coating compositions, from aqueous dispersions of compositions including advanced molecular weight epoxy-amine material and reactive diluent, may be prepared by polymerizing the reactive diluent.

The polymerization of the reactive diluents may be induced by any convenient method known in the art. Methods of initiating the polymerization 20 (e.g., thermally induced initiation, photochemically induced initiation) include, for example, the use of initiators (e.g., free radical initiators), or the use of ionizing radiation (e.g., electron beam irradiation). Preferably, initiators (e.g., free radical initiators) are used to initiate the polymerization of the reactive diluents.

← . 25 Free radical initiators may be added to coating compositions provided by the present invention to aid in the polymerization of the reactive diluents. Useful free radical initiators may be organic (e.g., organic peroxides) or inorganic (e.g., persulfates). Useful free radical initiators include, for example, peroxides, persulfates, persulfites, azoalkanes, and ultraviolet or visible light initiators.

30 Useful peroxide initiation systems include, for example, benzoyl peroxide, *tert*-butyl hydroperoxide, and a mixture of hydrogen peroxide and benzoin. Useful persulfate initiation systems include, for example, ammonium persulfate or

other alkali metal persulfates optionally combined with a suitable reducing agent. Suitable reducing agents include, for example, hydrazine, ammonium or alkali metal sulfites, bisulfites, metabisulfites, and hydrosulfites. Preferred free radical initiators include, for example, *tert*-butylhydroperoxide.

5 If a free radical initiator is used to initiate the polymerization of the reactive diluents, the temperature of the mixture may be adjusted as desired to allow the reaction to take place after the free radical initiator has been added. Preferably, the reaction temperature is at least 20°C, more preferably at least 25°C, and most preferably at least 30°C. Preferably, the reaction temperature is 10 at most 100°C, more preferably at most 90°C, and most preferably at most 85°C.

When a free radical initiator is used to initiate the polymerization, preferably a sufficient amount is used to effectively polymerize the reactive diluent. When a free radical initiator is used to initiate the polymerization of the reactive diluents, preferably at least 0.2% by weight and more preferably at least 15 0.4% by weight of the initiator is used based on the total weight of reactive diluents. When a free radical initiator is used to initiate the polymerization of the reactive diluents, preferably at most 3% by weight, more preferably at most 2% by weight, and most preferably at most 1% by weight of the initiator is used based on the total weight of reactive diluents.

20 *COATING COMPOSITIONS*

Coating compositions provided by the present invention preferably have useful properties for coating substrates. The coating compositions provided by the present invention are preferably aqueous dispersions that are stable for at least four months at ambient conditions. Preferably, stable coating compositions 25 are aqueous dispersions that do not exhibit a substantial change in viscosity or exhibit colloidal instability. Coatings made from stable aqueous dispersion preferably have substantially the same properties as when they are made.

Preferably, the waterborne coating compositions are substantially free of solvent. Waterborne compositions that are substantially free of solvent 30 preferably include at most 20% by weight solvent, more preferably at most 10% by weight solvent, and most preferably at most 5% by weight solvent, based on the total weight of the solids and solvent in the coating composition.

The aqueous dispersions provided by the present invention are preferably waterborne coating compositions. Waterborne coating compositions are advantageous in that they may have a low volatile organic compound (VOC) content. Waterborne coating compositions provided by the present invention 5 preferably have a volatile organic compound content of at most 0.2 kilograms per liter of solids, more preferably at most 0.1 kilograms per liter of solids, and most preferably at most 0.05 kilograms per liter of solids. When a volatile 10 organic acid is used in the preparation of the waterborne composition, the waterborne coating compositions preferably have a volatile organic compound content, excluding acid, of at most 0.2 kilograms per liter of solids, more preferably at most 0.1 kilograms per liter of solids, and most preferably at most 0.05 kilograms per liter of solids.

SUBSTRATES

Coating compositions provided by the present invention preferably are 15 useful for coating any substrate as desired. Preferably, substrates include, for example, cold rolled steel, zinc coated steel, aluminum, fiber boards, cement boards, plastics, paper, wood, and combinations thereof.

COATING APPLICATION, DRYING, AND CURING

Coating compositions provided by the present invention may be applied 20 to the desired substrate by any convenient method known in the art. Useful methods include, for example, spraying, roller coating, dip coating, curtain coating, brushing, electro coating, and combinations thereof.

Once the coating is applied to the substrate, the coating may be dried by any convenient method known in the art. Useful methods include, for example, 25 hot air drying (e.g., hot air ovens, air impingement drying, convection drying), exposure to microwave radiation, and exposure to infrared radiation. If the coating composition includes a crosslinker, the coating may optionally be cured during the drying process.

CURED COATING PROPERTIES

30 Preferably, the cured coatings provided by the present invention offer beneficial properties including, for example, chemical resistance, abrasion resistance, barrier properties, adhesion properties, and anti-corrosive properties.

Preferably, the cured coatings provided by the present invention are useful for applications including, for example, packaging coatings, anticorrosive coatings, stain blocker coatings, paper coatings, and cement board or plank coatings.

5 The present invention is illustrated by the following examples. It is to be understood that the particular examples, materials, amounts, and procedures are to be interpreted broadly in accordance with the scope and spirit of the invention as set forth herein.

10

EXAMPLES

Unless otherwise specified, all chemicals were commercially available from Sigma-Aldrich (St. Louis, MO).

All percentages refer to percentages by weight unless otherwise specified. All weights are given in grams (g) unless otherwise specified. All 15 molecular weights are weight average molecular weights unless otherwise specified.

EXAMPLE 1

An epoxy material available under the trade designation EPON 1004F 20 (902 g) from Resolution Performance Products (Houston, TX) was dissolved at 95-100°C in a mixture of styrene (214.6 g) and butylmethacrylate (214.6 g). An oxygen atmosphere was maintained over the mixture and 2,6-di-*tert*-butyl-4-methylphenol (0.74 g) was added to stabilize the vinyl monomers. The mixture was cooled to 70-75°C and diethanolamine (99.6 g) was added over a 30 minute period. After all the diethanolamine was added, the temperature was raised to 25 88-90°C and the temperature was maintained for 1.5 hours. The tertiary amine number was then determined to be 38.6. The batch was then cooled to 58-60°C and a blocked isocyanate available under the trade designation VESTANAT 31358/100 (357.8 g) from DeGussa Corp. (Parsippany, NJ) was added to the 30 batch followed by the addition of lactic acid (154.5 g, 88% by weight in water). The batch was mixed for 25 minutes before proceeding. Water (3787 g) was added to the batch under high agitation over a period of 30 minutes while

maintaining the temperature at 58-60°C. The batch was then stirred for 50 minutes at a temperature of 58-60°C before cooling the batch to 45-47°C. The atmosphere was then switched from air to nitrogen and a mixture of *tert*-butylhydroperoxide (9.34 g) and water (126.2 g) was added to the batch. After 5 the addition was complete, erythorbic acid (5.12 g) dissolved in water (126.2 g) was fed into the batch over a period of 20 minutes. The batch started to slowly exotherm after 5 minutes. The temperature was maintained below 57°C. After the erythorbic acid addition was complete, the batch was cooled to room temperature. The final dispersion had a solids content of 31.5% by weight.

10

EXAMPLE 2

An epoxy material available under the trade designation EPON 828 (1425 g) from Resolution Performance Products (Houston, TX) was mixed with Bisphenol A (285 g) from Resolution Performance Products (Houston, TX) and 15 ethyltriphenylphosphonium iodide (1.7 g, 95%) at room temperature. Under a nitrogen blanket, the mixture was gradually heated to 162°C over a time period of 2 hours and 15 minutes. Once the mixture reached 162°C the temperature was kept constant for 2 hours. At the end of this hold the batch was cooled to room temperature. Below a temperature of 124°C the nitrogen blanket was removed 20 and an oxygen atmosphere was created. Subsequently 2,6-di-*tert*-butyl-4-methylphenol (4.4 g) was added to the batch and a mixture of styrene (213.8 g) and butylmethacrylate (213.8 g).

EXAMPLE 3

25 The epoxy material prepared in Example 2 (333.62 g) was heated to 75°C in an oxygen atmosphere. Over a period of 90 minutes a mixture of diethanolamine (38.91 g) and n-butylamine (14.21 g) was added. During the addition of the amine mixture the temperature was allowed to rise to 93°C. At the end of the amine addition a mixture of styrene (6.63 g) and 30 butylmethacrylate (6.63 g) was added and the temperature was kept at 90 to 95°C for 3 hours and 20 minutes.

- The temperature was adjusted to 80°C then lactic acid (39.1 g, 85% by weight in water) was added. Over a period of 15 minutes 700 g of water was added while maintaining a temperature of 75 to 80°C. During this addition the oxygen atmosphere was replaced by a nitrogen atmosphere. When all water was added
- 5 n-butylacrylate (40.0 g) was mixed into the dispersion. The temperature was lowered to 45°C then a mixture of water (50.0 g) and *tert*-butylhydroperoxide (2.6 g) was added to the dispersion. Over a period of 25 minutes a solution of erythorbic acid (1.4 g) and water (50.0 g) was fed into the dispersion without external heating. After 15 minutes into this feed the temperature reached 54°C.
- 10 Once the erythorbic acid feed was completed the batch was cooled to room temperature. The product had a solids content of 36.9 % by weight.

EXAMPLE 4

The epoxy material prepared in Example 2 (333.62 g) was heated to

15 75°C in an oxygen atmosphere. Over a period of 90 minutes a mixture of diethanolamine (38.91 g) and n-butylamine (14.21 g) was added. During the addition of the amine mixture the temperature was allowed to rise to 93°C. At the end of the amine addition a mixture of styrene (6.63 g) and butylmethacrylate (6.63 g) was added and the temperature was kept at 90 to

20 95°C for 3 hours and 20 minutes.

The temperature was adjusted to 81°C then VESTANAT 31358/100 (106.6 g) from DeGussa Corp. (Parsippany, NJ) and hydroxyethyl methacrylate (6.0 g) were added. After 30 minutes of mixing at 81°C lactic acid (39.1 g, 85% by weight in water) was added. Over a period of 20 minutes 859 g of water was

← .25 added while allowing the temperature to drift from 81°C to 56°C. During this addition the oxygen atmosphere was replaced by a nitrogen atmosphere. When all water was added n-butylacrylate (34.0 g) was mixed into the dispersion. The temperature was lowered to 45°C then a mixture of water (50.0 g) and *tert*-butylhydroperoxide (2.6 g) was added to the dispersion. Over a period of 25 minutes a solution of erythorbic acid (1.4 g) and water (50.0 g) was fed into the dispersion without external heating. After 10 minutes into this feed the temperature reached 54°C. Once the erythorbic acid feed was completed the

batch was cooled to room temperature. The product had a solids content of 38.2 % by weight.

COATING PROPERTIES EVALUATION

5 Coatings made of the epoxy-acrylic hybrids of Examples 1, 3 and 4 were tested for adhesion properties and MEK resistance. Table 1 presents the formulas used to make the coatings.

TABLE 1: Formulas used for the epoxy-acrylic hybrids.

	Formula 1	Formula 2	Formula 3
Example 1 resin	100		
Example 3 resin		100	
Example 4 resin			100
Paraplex WP-1*	8.0		
butylglycol	4.0		4.0

10 * (polymeric plasticizer, Rohm & Haas)

Coatings were prepared by casting 5 mil-wet films of Formulas 1, 2 and 3 on various substrates. The coatings were allowed to dry for 15 minutes at room temperature and were then heated to 185°C for 30 minutes. The panels were 15 allowed to cool to room temperature prior to any testing.

TABLE 2: MEK double rub resistance.

Substrate	Formula 1	Formula 2	Formula 3
Bondrite B1000	100**	10	50
Bondrite B95	100	5	30
CRS Q-panel*	100	5	30

* cold rolled steel Q-panel

** at 100 MEK double rubs, the rubbing was stopped.

TABLE 3: Dry adhesion.

Substrate	Formula 1	Formula 2	Formula 3
Bondrite B1000	25*	0	0
Bondrite B95	0	0	10
CRS Q-panel	0	0	0

* Adhesion test performed according to ASTM D-3359 method B, percent coating loss reported.

5 TABLE 4: Wet adhesion after 24-hour water soak.

Substrate	Formula 1	Formula 2	Formula 3
Bondrite B1000	100*	0	0
Bondrite B95	0	0	25
CRS Q-panel	0	0	0

* Adhesion test performed according to ASTM D-3359 method B, percent coating loss reported.

The complete disclosure of all patents, patent applications, and
10 publications, and electronically available material cited herein are incorporated
by reference. The foregoing detailed description and examples have been given
for clarity of understanding only. No unnecessary limitations are to be
understood therefrom. The invention is not limited to the exact details shown
and described, for variations obvious to one skilled in the art will be included
15 within the invention defined by the claims.

What is claimed is:

1. A method of preparing a coating composition, comprising the steps of:
making an aqueous dispersion of a composition comprising an advanced molecular weight epoxy-amine material and a reactive diluent; and
polymerizing the reactive diluent to provide the coating composition.
2. The method of claim 1, further comprising the step of:
combining an amine and an epoxy material in the presence of a reactive diluent to provide the composition comprising an advanced molecular weight epoxy-amine material and a reactive diluent.
3. The method of claim 1, wherein the step of making the aqueous dispersion comprises combining the composition with an acid.
4. The method of claim 2, wherein the epoxy material is derived from Bisphenol A and epichlorohydrin.
5. The method of claim 2, wherein the epoxy material is dissolved or dispersed in the reactive diluent.
6. The method of claim 1, wherein the epoxy-amine material has residual epoxy functionality.
7. The method of claim 6, further comprising the step of:
reacting the epoxy-amine material having residual epoxy functionality with an active hydrogen compound or precursor.
8. The method of claim 7, wherein the step of reacting is carried out before the step of making the aqueous dispersion.

9. The method of claim 7, wherein the step of reacting is carried out after the step of making the aqueous dispersion.

10. The method of claim 7, wherein the step of reacting is carried out after the step of polymerizing the reactive diluent.

11. The method of claim 1, wherein the coating composition further comprises a crosslinker.

12. The method of claim 1, wherein the aqueous dispersion further comprises a surfactant.

13. The method of claim 3, wherein the composition is combined with a surfactant before combining the composition with the acid.

14. The method of claim 3, wherein the acid is an aqueous acid.

15. The method of claim 1, wherein the step of making the aqueous dispersion comprises:

combining the composition with an acid to provide an acidified composition; and

combining the acidified composition with an aqueous liquid.

16. The method of claim 15, wherein the aqueous liquid further comprises a surfactant.

17. The method of claim 1, wherein the reactive diluent comprises a multifunctional material.

18. The method of claim 1, further comprising the step of:
adding an additional reactive diluent before the polymerizing step.

19. The method of claim 1, wherein the reactive diluent is polymerized by free radical polymerization.
20. The method of claim 1, wherein the coating composition further comprises a solvent.
21. The method of claim 1, wherein the coating composition is a packaging coating composition, an anticorrosive coating composition, a stain blocker coating composition, a paper coating composition, a cement board coating composition, a fiberboard coating composition, and combinations thereof.
22. The method of claim 1, wherein the coating composition is substantially free of solvent.
23. The method of claim 1, wherein the coating composition has a volatile organic compound content of at most 0.2 kilograms per liter of solids.
24. The method of claim 3, wherein the coating composition has a volatile organic compound content, excluding acid, of at most 0.2 kilograms per liter of solids.
25. A coating composition prepared according to the method of claim 1.
26. A method of coating an article comprising the steps of:
 - applying a coating composition prepared according to the method of claim 1 to an article; and
 - hardening the coating composition to provide a coated article.
27. The method of claim 26, wherein the coating composition further comprises a crosslinker.

28. The method of claim 26, further comprising the step of heating the coated article to provide a crosslinked coating.
29. The method of claim 26, wherein the step of applying comprises applying the coating composition by an electro coat process.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/06969

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C09D163/00 C08L63/00 C09D5/44

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 7 C09D C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 932 636 A (NEUMANN UWE ET AL) 3 August 1999 (1999-08-03) claims 1,4,11; examples ---	1,3-16, 19-22, 25-29
X	US 6 201 043 B1 (GROSSE-BRINKHAUS KARL-HEINZ ET AL) 13 March 2001 (2001-03-13) claims 1-19; examples ---	1,3,4, 6-12, 14-16, 18,19, 21,22, 25-29
A	US 5 925 694 A (GODAU CLAUS ET AL) 20 July 1999 (1999-07-20) claim 1; examples -----	1-29



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
13 June 2003	27/06/2003

Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Marquis, D
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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/06969

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
US 5932636	A	03-08-1999	DE	4422869 A1		04-01-1996
			DE	4436093 A1		11-04-1996
			AT	185160 T		15-10-1999
			AT	184039 T		15-09-1999
			AU	686802 B2		12-02-1998
			AU	2332595 A		18-01-1996
			AU	688900 B2		19-03-1998
			AU	2332695 A		18-01-1996
			AU	688497 B2		12-03-1998
			AU	2332795 A		18-01-1996
			AU	2332895 A		18-01-1996
			AU	677101 B2		10-04-1997
			AU	7756594 A		18-05-1995
			BR	9404304 A		29-02-2000
			CA	2134723 A1		03-05-1995
			CA	2152427 A1		31-12-1995
			CA	2152428 A1		31-12-1995
			CA	2152433 A1		31-12-1995
			CA	2152434 A1		31-12-1995
			CN	1122322 A		15-05-1996
			CN	1120557 A		17-04-1996
			CN	1127264 A		24-07-1996
			CN	1122348 A		15-05-1996
			DE	59506718 D1		07-10-1999
			DE	59506933 D1		04-11-1999
			DE	59510390 D1		31-10-2002
			DK	694578 T3		19-05-2003
			EP	0656384 A2		07-06-1995
			EP	0694578 A2		31-01-1996
			EP	0698591 A1		28-02-1996
			EP	0698630 A1		28-02-1996
			EP	0694579 A2		31-01-1996
			ES	2137410 T3		16-12-1999
			FI	945118 A		03-05-1995
			HU	69052 A2		28-08-1995
			JP	8109149 A		30-04-1996
			JP	8100047 A		16-04-1996
			JP	8109241 A		30-04-1996
			JP	8100045 A		16-04-1996
			JP	7216085 A		15-08-1995
			US	5545678 A		13-08-1996
			US	5616634 A		01-04-1997
			US	6277944 B1		21-08-2001
			US	5708059 A		13-01-1998
US 6201043	B1	13-03-2001	DE	19633769 A1		26-02-1998
			CN	1230205 A		29-09-1999
			WO	9807794 A1		26-02-1998
			EP	0920480 A1		09-06-1999
			JP	2000516647 T		12-12-2000
US 5925694	A	20-07-1999	DE	19536381 A1		03-04-1997
			AT	228538 T		15-12-2002
			AU	6589596 A		10-04-1997
			CA	2186424 A1		30-03-1997
			DE	59609916 D1		09-01-2003
			EP	0770635 A2		02-05-1997
			JP	9111181 A		28-04-1997